

Prediction and evaluation of plasma arc reforming of naphthalene using a hybrid machine learning model

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Abstract

We develop a hybrid machine learning (ML) model for the prediction and optimization of a gliding arc plasma tar reforming process using naphthalene as a model tar compound from biomass gasification. A linear combination of three well-known algorithms, including artificial neural network (ANN), support vector regression (SVR) and decision tree (DT) has been established to deal with the multi-scale and complex plasma tar reforming process. The optimization of the hyper-parameters of each algorithm in the hybrid model has been achieved by using the genetic algorithm (GA), which shows a fairly good agreement between the experimental data and the predicted results from the ML model. The steam-to-carbon (S/C) ratio is found to be the most critical parameter for the conversion with a relative importance of 38%, while the discharge power is the most influential parameter to determine the energy efficiency with a relative importance of 58%. The coupling effects of different processing parameters on the key performance of the plasma reforming process has been evaluated. The optimal processing parameters are identified to achieve the maximum tar conversion (67.2%), carbon balance (81.7%) and energy efficiency (7.8 g/kWh) simultaneously when the global desirability index I_2 reaches the highest value of 0.65.

Keywords: Machine learning; Non-thermal plasma; Biomass gasification; Tar reforming; Naphthalene

1. Introduction

Biomass has been regarded as one of the most important renewable energy sources to meet the increasing energy demand as well as the mitigation of global climate change. Biomass gasification provides a sustainable and promising technical route for the production of high-value syngas (a mixture of H_2 and CO), which can be utilized to produce electricity, heat, chemicals, and fuels. However, the formation of undesirable contaminants (e.g. tars) in syngas remains a significant challenge to advance the gasification technology for large scale applications. Tar, consisting of a range of aromatic hydrocarbons with rings, causes serious operational problems, including blocking, corrosion, and crashing down the whole system. These tars contain a range of polycyclic aromatic hydrocarbons (PAHs), and some of them can be toxic and carcinogenic. The content of tars in the syngas can range from 1 g/Nm^3 up to 100 g/Nm^3 , limiting the use of syngas for gas turbine, fuel cells and chemical/fuel synthesis. Therefore, effective removal of tars in biomass gasification to produce high-quality and clean syngas is critical in biomass and bioenergy industry.

Non-thermal plasma (NTP) has been regarded as a promising and emerging technology for the synthesis of fuels and chemicals at low temperatures and ambient pressure [1–7]. Plasma processes can generate abundant energetic electrons and reactive species, which can break chemical bonds and rings of tar compounds, and enable thermodynamically unfavourable tar reforming to proceed at low temperatures. In addition, plasma processes can be operated responsively with the quick start-up and shut-down, which offers the flexibility to be integrated with renewable energy sources (e.g., wind and solar power) for distributed chemical energy storage, especially using surplus or intermittent electricity from renewable energy during peak moments on the grid. Up till now, the reported experimental studies mainly focused on the reforming of a range of tar model compounds, including toluene [8–13], benzene [14–16],

naphthalene [5,17–19], anthracene [20] and phenanthrene [21], using different plasma sources (e.g., dielectric barrier discharge (DBD) [22–24], gliding arc discharge (GAD) [4,8,25–29], and microwave (MW) plasma [30,31], etc.). However, plasma reforming of tars is a complex process and the process performance is influenced by a wide range of processing parameters [32,33]. Most of the previous works have simply investigated the effect of individual processing parameter on the plasma tar reforming, while no efforts have been dedicated to investigating the coupling effects of various parameters on the plasma reforming of tars, which is critical for the further optimization and development of plasma reforming technologies. Although plasma modelling can be helpful to understand the plasma reforming process to some extents, developing a plasma chemical kinetic model to predict and understand the plasma tar reforming process remains a significant challenge as the key reaction data (e.g., cross-section, rate constant) of large carbon molecules are not available. In addition, the multi-length-scale complexity in the plasma tar reforming process cannot be fully captured by plasma modeling.

Recently, machine learning (ML) has attracted increasing interest as a powerful tool for the prediction and optimization of a range of chemical processes. The use of ML for plasma gas conversions and air pollution control has also been explored. [34–38] Tu and co-workers developed a three-layer back-propagation (BP) artificial neural network (ANN) for the prediction of a complex plasma non-oxidative methane conversion process [34]. The discharge power was found to be the most important parameter in the plasma conversion of methane, while the excitation frequency of the plasma system was identified as the least important parameter affecting the plasma process. Zhu et al. developed a three-layer ANN model to get new insights into the effect of different operating parameters on the post-plasma catalytic removal of methanol [35]. The catalyst composition (i.e. Mn/Ce molar ratio of Mn-Ce oxide catalysts) was founded to be the most critical parameter determining the methanol removal

101 efficiency. Chang et al. developed an ANN model to better understand the effect of four
102 experimental parameters (discharge power, initial concentration of toluene, flow rate and
103 relative humidity) on the post-plasma catalytic removal of toluene over $\text{MnCoO}_x/\gamma\text{-Al}_2\text{O}_3$
104 catalysts [37]. A multi-objective optimization model was proposed to determine the
105 optimal experimental parameters using genetic algorithm (GA). However, using ML for
106 plasma chemical processes is still limited.

107
108 A variety of supervised ML algorithms are available for the prediction of chemical processes,
109 including plasma-based processes. Each algorithm has its strengths and weaknesses, and there
110 is no single ML algorithm that works the best on all supervised learning problems, including
111 regression and prediction problems. Artificial neural network (ANN), as one of the classic
112 supervised learning algorithms [39], has the advantages of self-adaptation, self-configuration,
113 and self-learning. ANN usually requires relatively large training data to avoid overfitting
114 problem and enhance the generalization capability. However, the experimental data sets are
115 often relatively small in plasma-based chemical processes as the process parameters in the
116 experiments are often varied within a narrow range due to the complexity of the plasma
117 chemical processes, and the relatively small data sets might lead to the instability of the
118 predicted result of the plasma process when using the ANN.

119
120 Meanwhile, other supervised learning algorithms, such as support vector machine (SVM) and
121 decision tree (DT), are also well-known for solving classification and regression problems
122 [40,41]. SVM algorithm can create a hyperplane to classify the data sets into different
123 categories, and then optimize the hyperplane by maximizing the margin between each data and
124 the hyperplane. This algorithm can efficiently handle both non-linear and high-dimensional
125 regression problems, also known as support vector regression (SVR), and has excellent

generalization capability to avoid overfitting of training data. However, the SVR algorithm often requires a relatively long training time with unsatisfied performance if the data sets are boisterous, which is likely to be the case for plasma chemical reactions. DT can solve regression problems by transforming a data set into a visualized tree representation, with an excellent noise tolerance character and strong robustness [42]. Thus, the DT algorithm has the advantages to deal with data sets with either limited samples or incomplete data. Compared to other ML algorithms, DT does not need pre-processing of data sets, such as normalization and standardization. However, the DT algorithm can easily cause over-fitting problems due to its weak generalization ability. It is also not effective to handle a complex system with large-scale data sets.

Clearly, choosing appropriate algorithm is essential to achieve the best performance of the ML model in solving a specific problem (e.g. prediction, optimization), especially when dealing with multi-scale, non-linear and complex chemical processes such as plasma tar reforming process. In the practical experiments, we often encounter some difficulties, such as long cycle time, complicated procedures and susceptibility to environmental interference, all of which cost us more time and resources to get the reliable results. In addition, experimental complexity scales exponentially with the number of variables, which restricts the number of experiments and narrows the range of process parameters. In some cases, the experimental complexity might lead to the following issues, such as large random error, missing data and bad points, etc., which make it difficult for the training of experimental data using a single ML algorithm. Hence, developing a hybrid ML model offers a promising solution for the fast and effective prediction and optimization of multi-scale and complex plasma processes with limited experimental data [43]. However, up till now, only ANN has been used for plasma-based chemical processes,

while the use of a hybrid ML model for the optimization of plasma chemical processes has not been reported yet.

In this work, a novel hybrid ML model combining ANN, SVR, and DT algorithms has been developed to predict and evaluate the critical performance of the plasma steam reforming of tar for the first time. Compared to the ML model using a single algorithm, the hybrid model combining three different algorithms can enhance the robustness and generalization ability of the ML model for the fast and effective prediction. In addition, genetic algorithm (GA) has been used to determine the optimal hyper-parameters of each algorithm (ANN, SVR, and DT) to enhance the adaptive ability and increase the accuracy of the prediction. Based on the well-trained hybrid model, the plasma tar reforming process has been analyzed to get new insights into the effect and relative importance of different process parameters, including discharge power, steam-to-carbon (S/C) ratio, and naphthalene concentration on the plasma reaction performance in terms of three key performance indicators (KPIs) including tar conversion, carbon balance and energy efficiency. The coupling effects of any two process parameters on the KPIs of the plasma process have also been evaluated. Furthermore, two indexes have been introduced to determine the optimal process parameters to maximize the key performance of the plasma tar reforming process.

2. Methodology and Experiment

2.1 Experimental method

A GAD reactor with two stainless-steel electrodes has been developed for plasma tar reforming [5]. The electrode gap was fixed at 2 mm for the initiation of the arc. Naphthalene (powder) was vaporized at 60-75 °C using a water bath and mixed with nitrogen. The mixed naphthalene and nitrogen flow (with or without steam) was preheated to 200 °C before injected into the

GAD reactor. The total gas flow rate was maintained at 4 L/min, and the inlet concentration of naphthalene can be controlled between 1.1 mg/L and 1.7 mg/L. The steam-to-carbon (S/C) ratio can be varied between 0 and 4.0 to investigate the role of steam in the plasma reforming of naphthalene. The GAD reactor was connected to an alternating current high voltage transformer (10 kV/50 Hz). The electrical signals (arc voltage U and arc current I) were recorded using a digital oscilloscope (Tektronix, MDO3024). The discharge power was determined through the integration of arc voltage and arc current in a cycle T .

$$\text{Discharge power } (W) = \frac{1}{T} \int_0^{t=T} U(t) \times I(t) dt \quad (1)$$

The gaseous products were measured and quantified using gas chromatography (Agilent 7820A) fitted with a flame ionization detector and a thermal conductivity detector. A Molecular Sieve 5A column (HP MOLESIEVE) was used for the measurement of CO and H₂, and an HP-PLOT/Q column was used to separate CO₂, CH₄, and C₂-C₄ hydrocarbons. The liquid products were condensed and dissolved in dichloromethane using a cold trap.

The conversion of naphthalene is defined as

$$X_{C_{10}H_8} (\%) = \frac{C_i - C_o}{C_i} \times 100\% \quad (2)$$

Where C_i is the inlet concentration of naphthalene, and C_o is the concentration of naphthalene after the plasma reaction.

The converted rate is defined as

$$R_{C_{10}H_8} (\text{mg/min}) = C_i \times X_{C_{10}H_8} (\%) \times \text{Total flow rate (L/min)} \quad (3)$$

The carbon balance of the plasma tar reforming process is given by

Without steam

$$\text{Carbon balance} (\%) = \sum \frac{\text{Produced } C_xH_y (x=1, 2, 3, 4)}{\text{Converted } C_{10}H_8} \times 100\% \quad (4)$$

With steam

$$\text{Carbon balance}(\%) = \sum \frac{\text{Produced } C_xH_y (x=1, 2, 3, 4) \text{ and } CO_x (x=1, 2)}{\text{Converted } C_{10}H_8} \times 100\% \quad (5)$$

The energy efficiency for tar conversion is defined as:

$$E(\text{g/kWh}) = \frac{\text{Mass of converted tar (g/h)}}{\text{Discharge power (kW)}} \quad (6)$$

Non-dimensional indexes, I_1 & I_2 ($0 < I_1, I_2 < 1$), are defined to evaluate the effectiveness of the plasma tar reforming process. Specifically, I_1 is defined as the product of the normalized (N) tar conversion and carbon balance to evaluate the effective conversion of $C_{10}H_8$ (Eq. 7). I_2 is defined as the product of three normalized KPIs to determine the optimal process parameters to maximize the conversion, carbon balance and energy efficiency simultaneously (Eq. 8). All the normalized parameters are in the range of 0-1.

$$I_1 = N(\text{tar conversion}) \times N(\text{carbon balance}) \quad (7)$$

$$I_2 = N(\text{tar conversion}) \times N(\text{carbon balance}) \times N(\text{energy efficiency}) \quad (8)$$

2.2 Description of the hybrid model

The key reaction performance (P) of the plasma tar reforming process was simulated using a hybrid ML model via a linear combination of ANN, SVR and DT algorithms, as shown in Eq. 9.

$$P = W_1 \times P_{\text{ANN}} + W_2 \times P_{\text{SVR}} + W_3 \times P_{\text{RT}} \quad (0 \leq W_1, W_2, W_3 \leq 1) \quad (9)$$

Where W_1 , W_2 and W_3 are the relative weight of ANN, SVR and DT algorithms, respectively.

The mean squared error (MSE), one of the most common criteria, is defined as the mean difference between the experimental data (R_i) and the predicted results (P_i),

$$\text{MSE} = \frac{1}{n} \sum_{i=1}^n (P_i - R_i)^2 \quad (10)$$

In this study, the MSE can be used to evaluate the performance of the hybrid ML model in the optimization of the relative weight for each algorithm using an exhaustion method. The

optimal relative weight for each algorithm in the hybrid model is achieved when the minimum MSE of the ML model is reached.

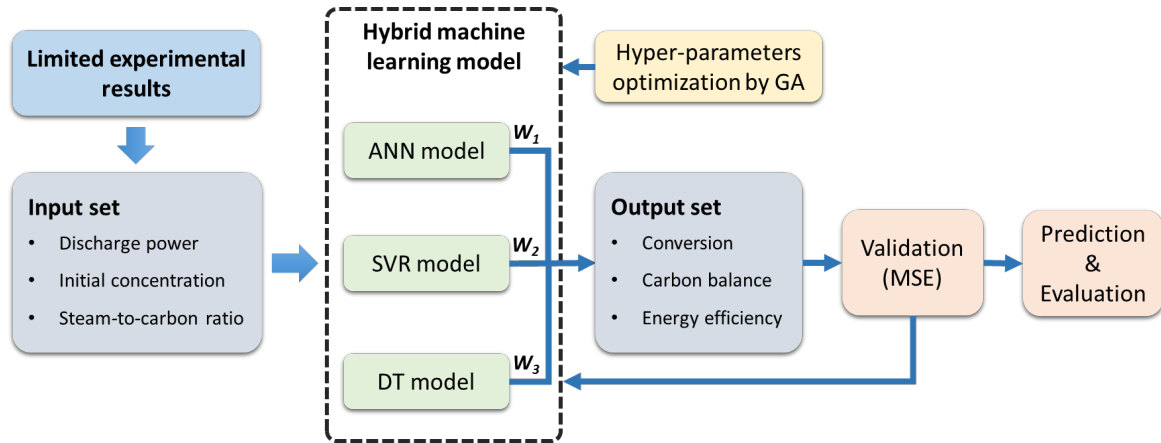


Figure 1 Scheme of the logical structure for the prediction and evaluation using the hybrid ML model.

Figure 1 shows the logical structure for the prediction, evaluation and optimization using this hybrid ML model. Three key processing parameters, including discharge power, inlet $C_{10}H_8$ concentration and steam-to-carbon ratio (S/C) are taken into account and used as the input in the model. The conversion of naphthalene, carbon balance and energy efficiency are selected as the KPIs in this study. GA is applied to optimize the hyper-parameters of these three algorithms (ANN, SVR and DT) in the hybrid ML model, such as the learning rate for ANN, the variable C and γ (Radial Basis Function (RBF) kernel) for SVR and the depth for DT.

2.2.1 Artificial neural network

For the ANN model, Adaline (Adaptive linear neuron, Figure 2), a single-layer neural network, was developed to simulate the plasma tar reforming process. The model includes three key process parameters as the inputs, including discharge power (X_1), inlet $C_{10}H_8$ concentration (X_2) and S/C ratio (X_3). Bias (b) is a basic parameter in the neural network, which can be used to

adjust the output along with the weighted sum of the inputs to the neuron. The bias can be used to shift the activation function ($\sigma(z)$) and offset the predicted results, enhancing the flexibility and generalization of the ANN model. Z-score normalization has been used to pre-process all data sets, including the input process parameters and the predicted KPIs.

In this case, the cost function ($J(w)$, Eq. 11) is determined as the sum of squared errors (SSE) between the predicted results ($\sigma(z^{(i)})$) and the experimental data ($y^{(i)}$), and can be minimized using a gradient descent algorithm to get the optimized weight for each processing parameter (inputs).

$$J(w) = \frac{1}{2} \sum_i \left(y^{(i)} - \sigma(z^{(i)}) \right)^2 \quad (11)$$

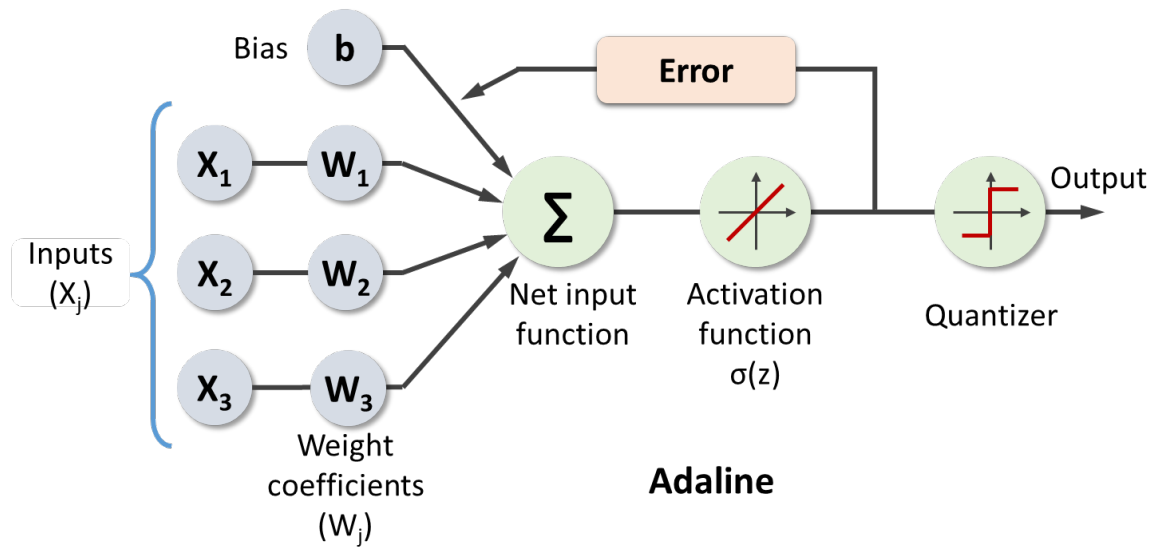


Figure 2 Scheme of an adaptive linear neuron (Adaline).

2.2.2 Support vector regression

The SVR is a robust learning algorithm and has been widely used to solve aggression problems with small samples, high-dimensions and non-linear. It can be formulated as an optimization problem (Eq. 12) to minimize the norm of the weight vector (w) with some slack variables (ξ_i).

and ξ_i^*) introduced to increase the tolerance of regression errors. With a Lagrange dual formulation, the optimization (Eq. 12) can be alternatively done by solving its dual problem (Eq. 13).

$$\min_{w,b,\xi,\xi^*} \frac{1}{2} \|w\|^2 + C \sum_{i=1}^m (\xi_i + \xi_i^*), \quad \xi_i, \xi_i^* \geq 0, i=1, \dots, m \quad (12)$$

$$\max \sum_{i=1}^m y_i (\alpha_i^* - \alpha_i) - \varepsilon \sum_{i=1}^m (\alpha_i^* + \alpha_i) - \frac{1}{2} \sum_{i,j=1}^m (\alpha_i^* - \alpha_i) (\alpha_i^* + \alpha_i) x_i^T x_j \quad (13)$$

Where C is the penalty term to determines the trade-off between the misclassifications of the training data and the width of the margin. α_i and α_i^* are the Lagrange multipliers, and ε is the tolerance of margin.

In this study, the RBF kernel function (Eq. 14) has been used in the SVR model to plot the process parameters and KPIs for effective and accurate prediction of the performance in the plasma tar reforming process.

$$K(x_i, x_j) = \exp\left(-\gamma \|x_i - x_j\|^2\right), \quad \gamma > 0 \quad (14)$$

where γ defines the influence of a single sample on the entire classification hyperplane. Then, the generic equation of the SVR model based on the RBF kernel function can be described as:

$$f(x) = \sum_{i=1}^m (\alpha_i^* - \alpha_i) K(x_i, x) + b \quad (15)$$

Where b refers to the bias term.

GA is used to find the optimal hyper-parameters (γ and C) in the SVR training process when the minimum MSE for each KPI is reached. One hundred iterations are used in the optimization of the hyper-parameters using GA, with the hyper-parameters (γ and C) being chosen in the range of $0 < \gamma < 1$ and $0 < C < 10^4$, respectively. In this study, the optimized hyper-parameter

(γ , C) of the SVR model is (1126, 0.56) for three KPIs. The SVR algorithm was developed using the “Scikit-learn” library in Python.

2.2.3 Decision tree

A standard binary decision tree for solving this regression problem is defined with several branches, one root, a few nodes and leaves. Basically, one branch is a chain of nodes from root to a leaf, and each node refers to one attribute. The splitting criteria for this regression tree, which is also known as CART (classification and regression tree), is the MSE, which has been defined in Eq. 10. For each node, the algorithm will calculate the predicted value and calculate the MSE for each subset, and the regression tree will evolve by seeking the smallest MSE value. In our model, a maximum depth of the tree has been set to achieve high accuracy for the prediction of the three KPIs. The DT algorithm was also developed using the “Scikit-learn” library.

3. Results and discussion

3.1 Optimization of the hybrid ML model

Figure 3 shows the influence of the relative weights for each algorithm on the MSE of the hybrid ML model. When the ML model uses a single algorithm, the MSE of the model is 0.110, 0.107 and 0.068 for ANN, SVR and DT, respectively. These values are much higher than the minimum MSE (0.043) of the hybrid model, indicating that the optimized hybrid ML model is much superior to the models using a single algorithm in this study. The optimal weight of ANN, SVR and DT in this hybrid model is 0.31, 0.10, and 0.59, respectively. Thus, the optimal hybrid model can be expressed as:

$$\text{Hybrid model: } P = 0.31 \times P_{\text{ANN}} + 0.1 \times P_{\text{SVR}} + 0.59 \times P_{\text{DT}} \quad (16)$$

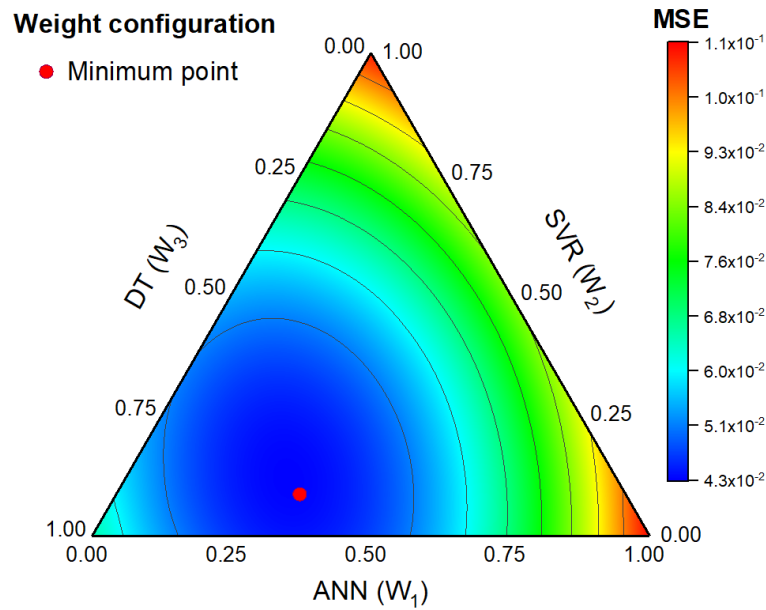


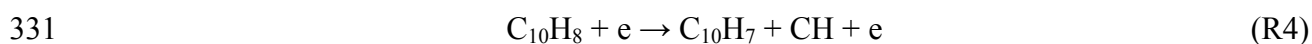
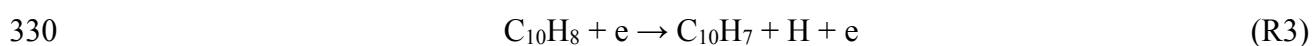
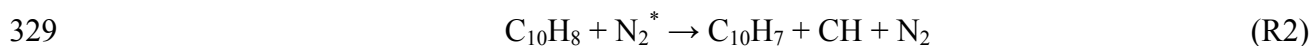
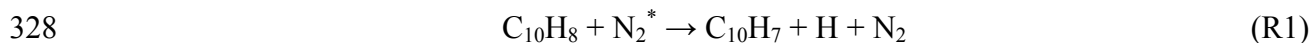
Figure 3 Effect of the relative weights of ANN, SVR, and DT on the MSE for the predicted output set of KPIs.

3.2 Output prediction and model validation

Figure 4 shows a comparison between the experimental and simulated naphthalene conversion in the plasma reforming reaction without steam ($S/C = 0$). The predicted results obtained from the hybrid ML model reasonably well agree with those from the experiment. Hence, the model can be used to predict the reaction performance. For example, the conversion of naphthalene is predicted to be 72% at an inlet $C_{10}H_8$ concentration of 1.4 mg/L. At a higher tar concentration (e.g., $>1.4 \text{ g/Nm}^3$), the change of tar concentration has a weak effect on the conversion of naphthalene. By contrast, the converted rate of naphthalene was increased continuously from 3.7 to 5.6 mg/min with the increase of inlet $C_{10}H_8$ concentration from 1.1 to 2.0 g/Nm^3 . In addition, the discharge power shows a limited effect on the conversion of naphthalene in the reaction without steam. With the increase of discharge power, the predicted converted rate remained stable at around 4.7 mg/min, indicating that the discharge power had a limited effect on the performance of plasma processing of naphthalene.

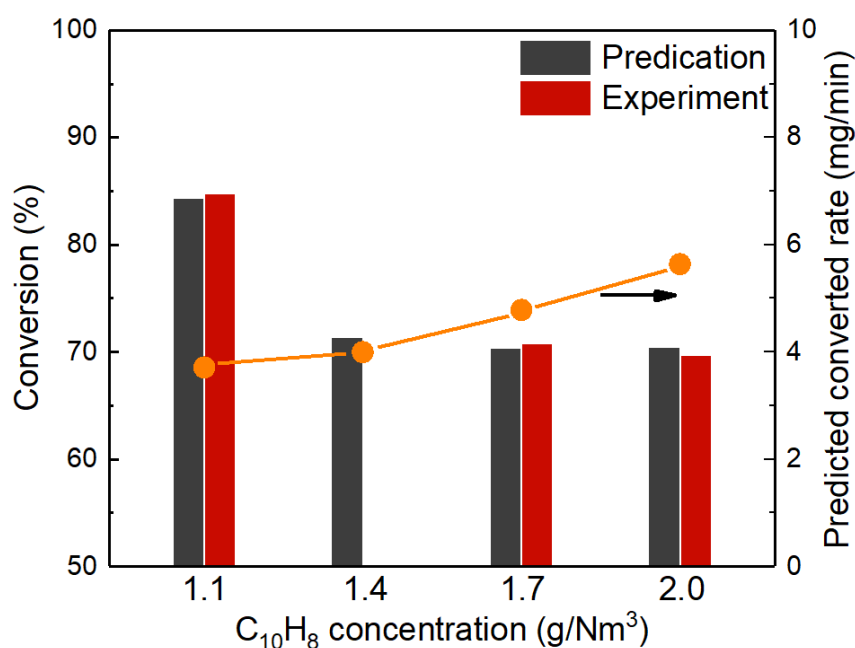
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324 As previously reported, the key reaction channels in the plasma reforming of naphthalene are
 325 dehydrogenation and one ring-open reaction. In these two reactions, the initial dissociation of
 326 naphthalene can proceed via the collisions of naphthalene with excited nitrogen species N_2^*
 327 (e.g., $N_2(A^3\Sigma^+)$) and energetic electrons (R1-R4) [5,27].



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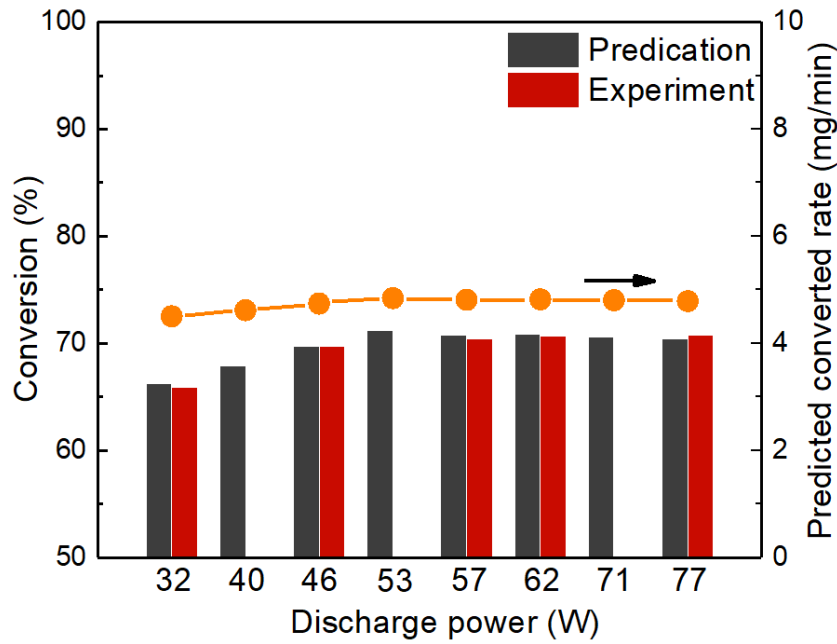
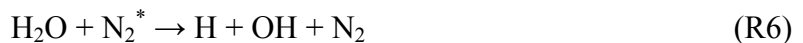


Figure 4 (a) Effect of inlet $C_{10}H_8$ concentration on the conversion and predicted converted rate (discharge power = 77 W, S/C = 0); (b) Effect of discharge power on the conversion and predicted converted rate ($C_{10}H_8$ concentration = 1.7 g/Nm^3 , S/C = 0).

Figure 5 shows the predicted values are in agreement with the experimental results at different S/C ratios and discharge powers. As shown in Figure 5a, the conversion of naphthalene in the plasma steam reforming of tar gradually increases when increasing S/C ratio, reaching a peak of 84.5% at an S/C ratio of 2.0 (Figure 5a). However, the conversion of naphthalene drops by about 20% when further increasing the S/C ratio from 2.0 to 4.0. In this study, the optimal S/C ratio is found to be 2.0 to achieve the highest conversion of naphthalene. Due to the presence of steam in the plasma reforming process, abundant OH radicals can be produced via H_2O dissociation by energetic electrons (R5) and excited N_2 species (N_2^*) (R6) [5]. The OH radicals are highly oxidative and can further oxidize naphthalene (R7) at a relatively high rate constant ($1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).



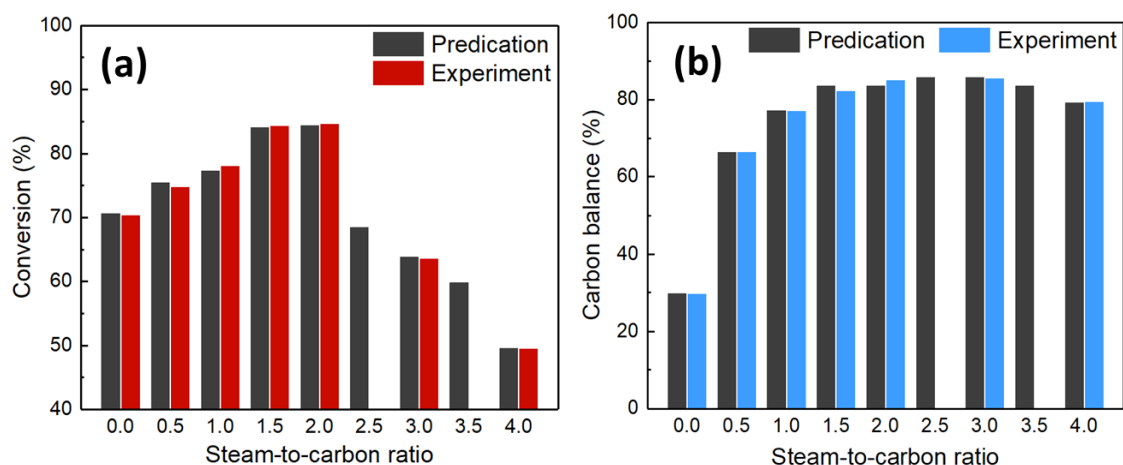
352 $C_{10}H_8 + OH \rightarrow \text{products}$ (R7)

353 However, adding excessive H_2O (e.g. at a higher S/C ratio) to the plasma tar reforming process
 354 consumes a large number of energetic electrons due to the electron attachment effect of water,
 355 which in turn negatively affects the conversion of naphthalene. Thus, choosing the appropriate
 356 S/C molar ratio is critical to maximizing the performance of the plasma steam reforming
 357 process.

358 Moreover, the carbon balance increases significantly from 30% to 66% when adding steam
 359 into the reaction, but only weakly changes with the change of the S/C ratio (Figure 5b). The
 360 presence of steam in the plasma reforming reaction enhances the oxidation of naphthalene and
 361 its intermediates due to the formation of OH radicals, thus reducing the carbon deposition. In
 362 addition, we find that the energy efficiency of the plasma tar reforming process as a function
 363 of the S/C ratio follows the same evolution as the conversion of naphthalene (Figure 5c).

364
 365 Figure 5d-5f shows the effect of discharge power on the three KPIs with an S/C ratio of 2.0.
 366 Increasing the discharge power gradually enhances the conversion of naphthalene but decreases
 367 the energy efficiency of the plasma process. At a low discharge power (< 45 W), the influence
 368 of discharge power on the conversion of naphthalene is not so substantial.

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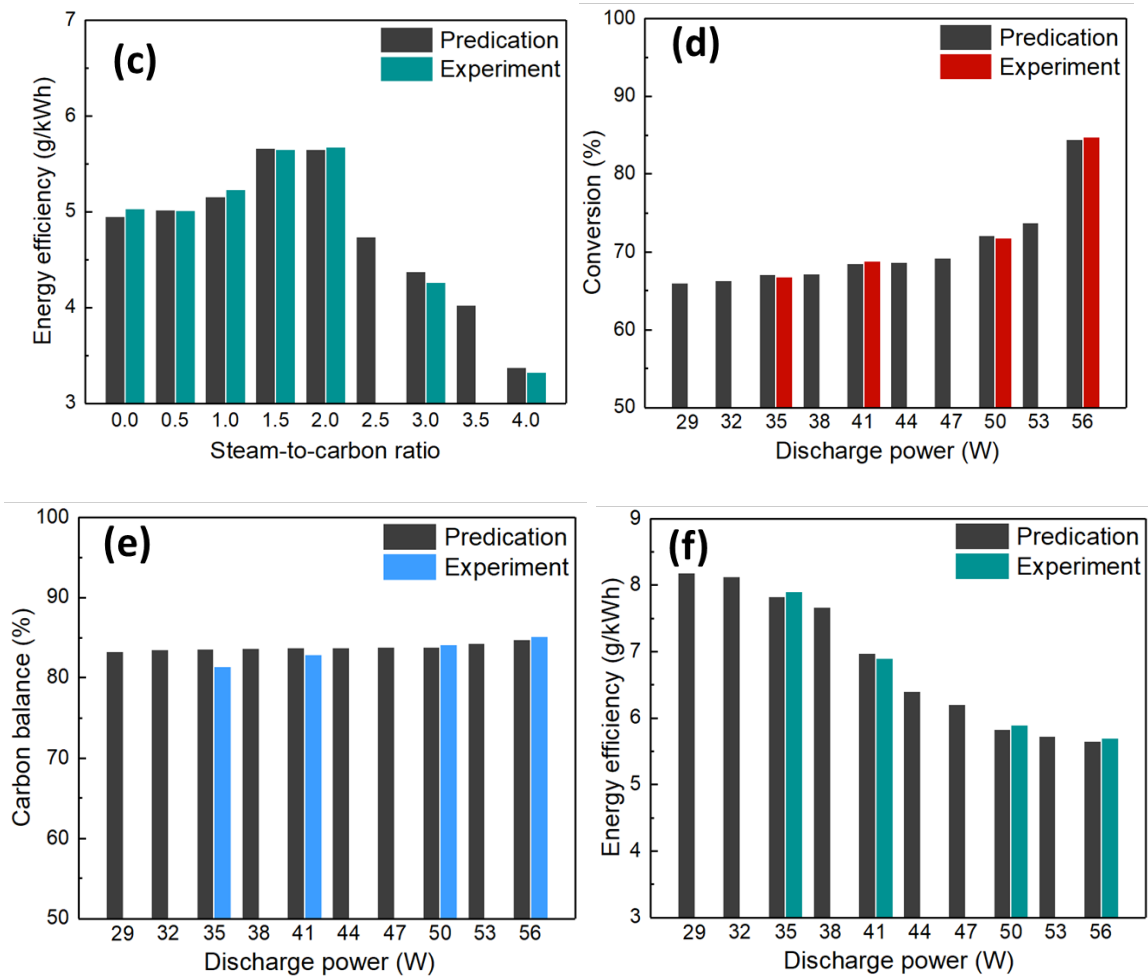


Figure 5 Effect of S/C ratio on (a) tar conversion, (b) carbon balance and (c) energy efficiency (discharge power = 57 W, concentration = 1.7 g/Nm³); Effect of discharge power on (d) tar conversion, (e) carbon balance and (f) energy efficiency (C₁₀H₈ concentration = 1.7 g/Nm³, S/C ratio = 2.0).

In this study, 20% of the experimental data were selected randomly as a test set to validate the hybrid model using GA. The regression plots for the comparison between the experimental and simulated KPIs are presented in Figure 6. The solid line represents the simulated results are equal to the experimental data. The experimental data show a fairly good agreement with the results simulated from the hybrid model for all three KPIs, as evidenced by the high correlation coefficients (R^2) of 0.997 (conversion), 0.998 (carbon balance), and 0.997 (energy efficiency).

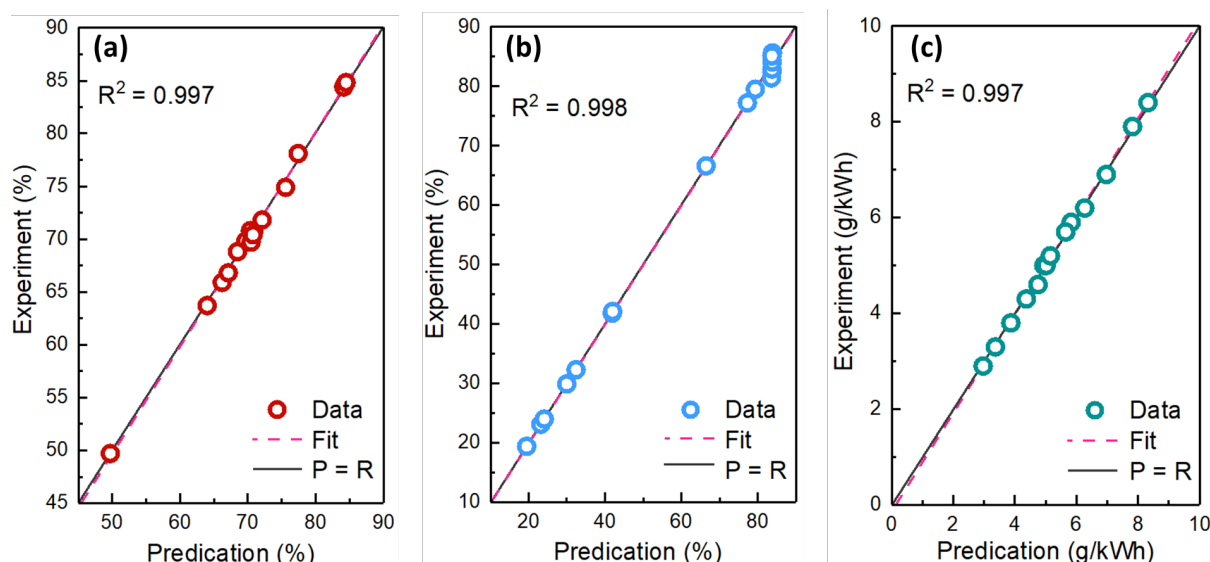


Figure 6 Regression plots for (a) conversion, (b) carbon balance, and (c) energy efficiency using the hybrid prediction model.

3.3 Importance of different process parameters

Figure 7 shows the relative importance of different operating parameters in the plasma steam reforming of naphthalene. The S/C ratio is found to be the most critical parameter affecting the conversion of naphthalene with a relative importance of 48%. Moreover, the relative importance of S/C ratio and discharge power for the carbon balance is over 40%, which indicates that both parameters significantly affect the carbon balance. For the energy efficiency, the discharge power shows much higher importance of ~58% compared to other two process parameters, suggesting that the discharge power is the most important parameter to determine the energy efficiency of the plasma process for naphthalene conversion. Note that the relative importance of the inlet naphthalene concentration is 13-16% for all three KPIs. These findings show that the input concentration of naphthalene in the range of 1.0 - 2.0 g/Nm³ makes the least contributions to this plasma steam reforming process.

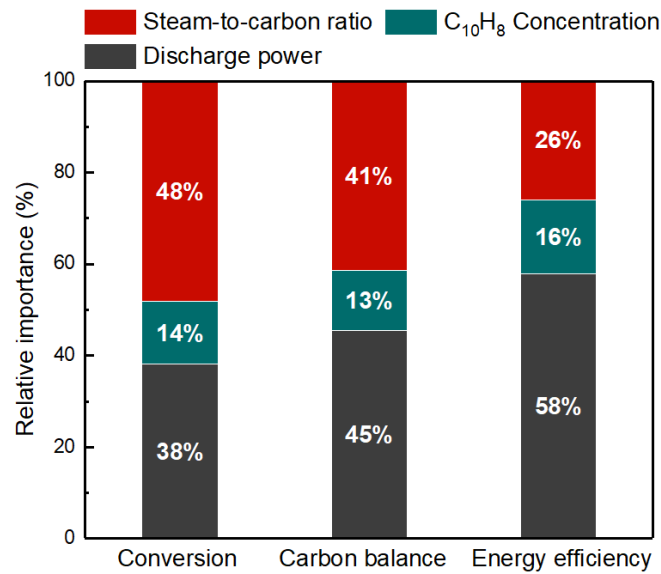


Figure 7 Relative importance (%) of different process parameters in the plasma-driven steam reforming of naphthalene.

3.4 Coupling effect of process parameters

The validation of the hybrid ML model enables us to investigate the interactions between the process parameters on the KPIs of the plasma reforming process. As shown in Figure 8a, in the plasma reforming of naphthalene without steam ($S/C = 0$), the conversion of naphthalene can be enhanced by lowering the input concentration and increasing the discharge power in the range of 1.0 - 1.3 g/Nm³ and 55 - 80 W, respectively, with the highest naphthalene conversion being achieved at 84%. Figure 8b shows that the carbon balance is almost unchanged when the discharge power is lower than 50 W regardless of the change of the naphthalene concentration. However, at a discharge power of >50 W (especially > 60 W), increasing the discharge power substantially enhances the carbon balance if the concentration is in the range of 1.8 - 2.0 g/Nm³, but slightly decreases the carbon balance at a lower naphthalene concentration (1.0 - 1.4 g/Nm³). Also, the predicted energy efficiency monotonically decreases with the increase of discharge power at a constant naphthalene concentration, as shown in Figure 8c. The highest energy

efficiency of the plasma process is predicted to be 8.2 g/kWh at 35 W with an inlet naphthalene concentration of 1.7 g/Nm³.

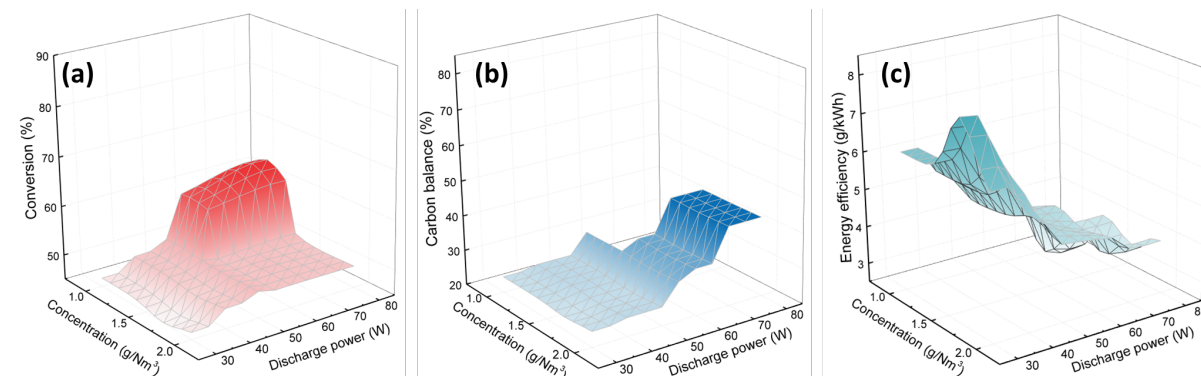


Figure 8 Prediction effects of the interaction between naphthalene concentration and discharge power on (a) tar conversion, (b) carbon balance, and (c) energy efficiency without steam. (S/C = 0)

In the plasma steam reforming of naphthalene, the interaction between the S/C ratio and discharge power on different KPIs is shown in Figure 9. The effect of discharge power and S/C ratio on the conversion shows a ridge-shaped surface, with the maximum conversion being achieved at an S/C ratio of 1.0-2.0. In contrast, the highest conversion of naphthalene is predicted to be 89% at a discharge power of 70 W and an S/C ratio of 2.0. Compared to the discharge power, the S/C ratio has a more significant effect on the carbon balance, as shown in Figure 9b. The carbon balance can reach the highest value of 85.5% at an S/C ratio of 2.0-3.0. Figure 9c shows higher energy efficiency can be expected when lowering both the discharge power and S/C ratio. The maximum energy efficiency can be around 8.0 g/kWh with the minimum discharge power (30 W) and the S/C ratio (S/C = 0). Meanwhile, when the discharge power is greater than 50 W, the energy efficiency can be optimized and maximized at an S/C ratio of 2.0, indicating that adding a moderate amount of steam to the plasma process could enhance the energy efficiency.

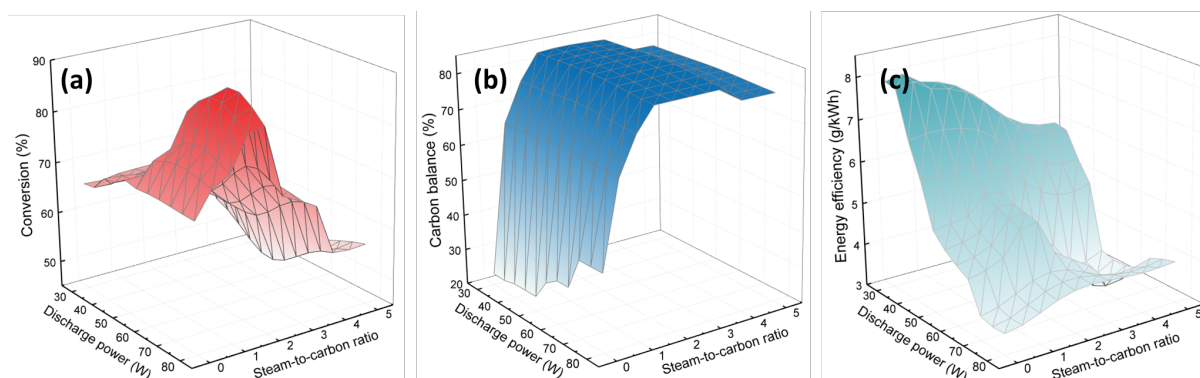


Figure 9 Prediction effects of the interaction between discharge power and steam-to-carbon ratio on (a) conversion, (b) carbon balance and (c) energy efficiency in the steam reforming reaction (concentration = 1.7 g/Nm^3).

Furthermore, the sliced graphs of the predicted results show the simultaneous effects of discharge power, S/C ratio, and inlet naphthalene concentration on the three KPIs (Figure 10a-10c). When the inlet C_{10}H_8 concentration is lower than 1.3 g/Nm^3 , the conversion can reach more than 80% in the optimal ranges of discharge power (60-80 W) and S/C ratio (0-2.0). To achieve a high naphthalene conversion ($> 80\%$) at a high C_{10}H_8 concentration ($> 1.4 \text{ g/Nm}^3$), the S/C ratio needs to be narrowed between 1.0 and 2.0 (Figure 10a).

Carbon balance shows a similar trend under the coupling effects of these three operating parameters (discharge powers, S/C ratios and tar concentration). A carbon balance of $> 80\%$ can be obtained if the tar concentration is in the range of $1.6\text{-}1.8 \text{ g/Nm}^3$ (Figure 10b). As shown in Figure 10c, the energy efficiency of the plasma reforming process is mainly affected by the discharge power, rather than the inlet C_{10}H_8 concentration and S/C ratio. Lower discharge power (30-40 W) is favourable to achieve higher energy efficiency. The highest energy efficiency ($\sim 8.4 \text{ g/kWh}$) can be obtained when the discharge power, C_{10}H_8 concentration and S/C ratio are 30 W, 1.7 g/Nm^3 , and 0.6, respectively (Figure 10c).

460

461 Clearly, the overall performance of plasma steam reforming of naphthalene strongly depends
462 on a range of plasma processing parameters. It is essential to optimize the complex plasma-
463 enhanced tar reforming process with multiple input processing parameters and multiple KPIs.
464 In this work, I_1 has been used to determine the optimal processing parameters to maximize the
465 effective conversion of naphthalene for process optimization. As shown in Figure 10d, at a
466 $C_{10}H_8$ concentration of 1.5-1.9 g/Nm³, I_1 can be higher than 0.60 if the discharge power and
467 S/C ratio are in the optimal range of 60-80 W and 1.5-2.0, respectively. The highest I_1 of 0.69
468 can be obtained at a discharge power of 60 W, an inlet concentration of 1.7 g/Nm³ and an S/C
469 ratio of 2.0.

470

471 In addition, I_2 , also known as a global desirability function [44], has been introduced to
472 determine the optimal processing parameters to maximize both effective tar conversion and
473 energy efficiency simultaneously in the plasma-enhanced tar reforming process. Figure 10e
474 shows that relatively high I_2 (> 0.5) can be obtained when the inlet naphthalene concentration
475 and S/C ratio are in the optimal range of 1.5-1.9 g/Nm³ and 1.5-3.5, respectively when the
476 discharge power is 30-45 W. Furthermore, when I_2 reaches the highest value of 0.65, the
477 optimal discharge power (35 W), input $C_{10}H_8$ concentration (1.7 g/Nm³) and S/C ratio (2.0) are
478 determined to achieve the maximum KPIs - conversion (67.2%), carbon balance (81.7%) and
479 energy efficiency (7.8 g/kWh) simultaneously in the plasma reforming of naphthalene.

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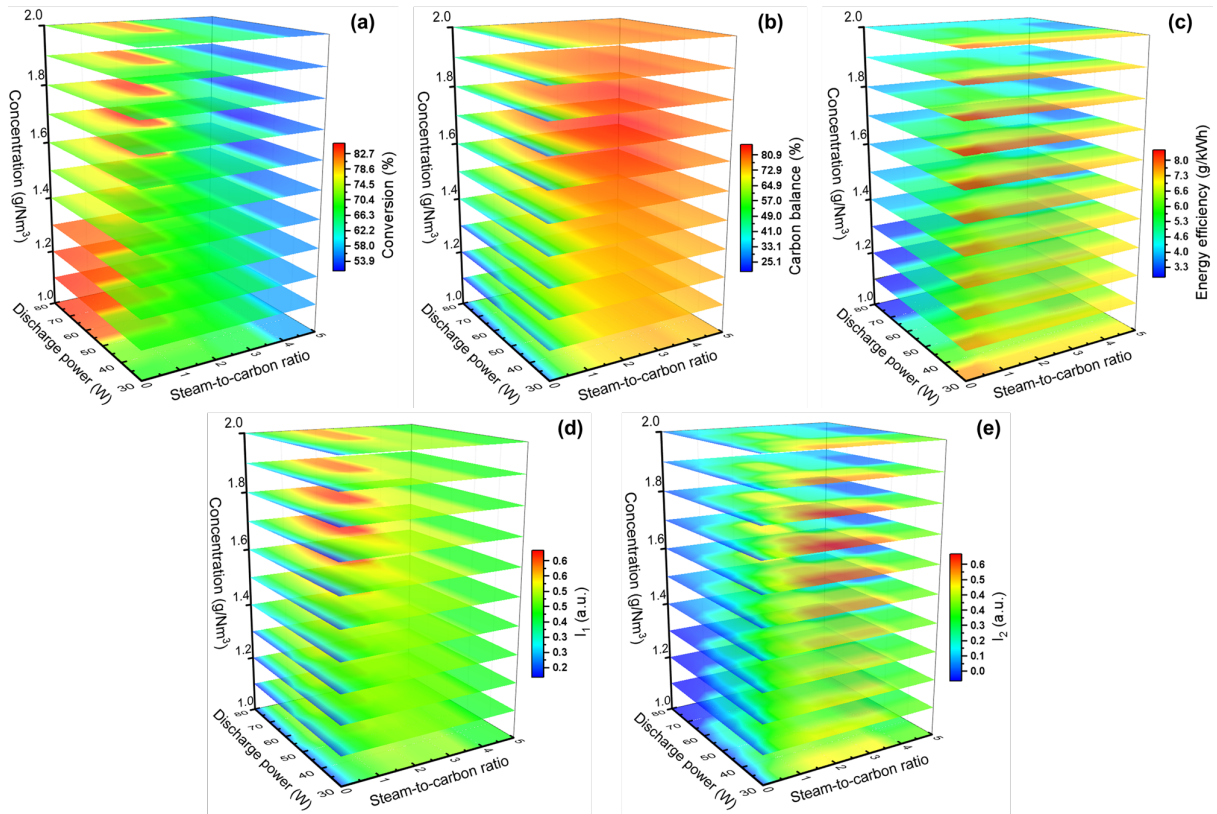


Figure 10 Prediction effects of the three-body interactions of discharge power, steam-to-carbon ratio and inlet $C_{10}H_8$ concentration on (a) conversion, (b) carbon balance and (c) energy efficiency; and the comprehensive evaluation indexes (d) I_1 and (e) I_2 .

4. Conclusions

A well-trained hybrid ML model incorporating three different algorithms (ANN, SVR and DT) has been developed to predict and evaluate the influence of different processing parameters (discharge power, tar concentration and S/C ratio) on the KPIs (tar conversion, carbon balance and energy efficiency) of the multi-scale and complex plasma tar reforming process. The hyper-parameters of each algorithm in the hybrid ML model have been optimized with the GA. The predicted results from the model agree very well with the experimental data, as confirmed by the high regression coefficient of 0.997. Both of the S/C ratio and the discharge power are identified as the most critical parameters affecting the three KPIs, while the inlet concentration

of naphthalene is less critical compared to the other two parameters. The hybrid model shows that the discharge power is the most important processing parameter to determine the energy efficiency of the plasma process with a relative importance of 58%, while the S/C ratio is the most critical parameter for the tar conversion with a relative contribution of 38%. When I_2 reaches the highest value of 0.65, the optimal discharge power (35 W), input $C_{10}H_8$ concentration (1.7 g/Nm^3) and S/C ratio (2.0) are obtained to maximize three KPIs - conversion (67.2%), carbon balance (81.7%) and energy efficiency (7.8 g/kWh) simultaneously in the plasma reforming of naphthalene. This work has demonstrated that a well-trained hybrid ML model can provide effective, accurate and fast prediction and optimization of the plasma tar reforming process, and has great potential to be used for a range of plasma-based chemical processes.

Acknowledgements

This project has received funding from European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 722346. The support from the Royal Society's Newton Advanced Fellowship (Ref. NAF/R1/180230) is greatly appreciated.

References

- [1] A. Bogaerts, X. Tu, J.C. Whitehead, G. Centi, L. Lefferts, O. Guaitella, F. Azzolina-jury, H. Kim, A.B. Murphy, W.F. Schneider, T. Nozaki, C. Jason, A. Rousseau, F. Thevenet, A. Khacef, The 2020 plasma catalysis roadmap, J. Phys. D. Appl. Phys. 53 (2020) 443001. doi:10.1088/1361-6463/ab9048.

- 520 [2] A. George, B. Shen, M. Craven, Y. Wang, D. Kang, C. Wu, X. Tu, A review of non-
521 thermal plasma technology: A novel solution for CO₂ conversion and utilization,
522 *Renew. Sustain. Energy Rev.* 135 (2021) 109702. doi:10.1016/j.rser.2020.109702.
- 523 [3] L. Liu, Z. Zhang, S. Das, S. Kawi, Reforming of tar from biomass gasification in a
524 hybrid catalysis-plasma system: A review, *Appl. Catal. B Environ.* 250 (2019) 250–
525 272. doi:10.1016/j.apcatb.2019.03.039.
- 526 [4] S. Liu, D. Mei, L. Wang, X. Tu, Steam reforming of toluene as biomass tar model
527 compound in a gliding arc discharge reactor, *Chem. Eng. J.* 307 (2017) 793–802.
528 doi:10.1016/j.cej.2016.08.005.
- 529 [5] Y. Wang, H. Yang, X. Tu, Plasma reforming of naphthalene as a tar model compound
530 of biomass gasification, *Energy Convers. Manag.* 187 (2019) 593–604.
531 doi:10.1016/j.enconman.2019.02.075.
- 532 [6] D. Mei, Y. Wang, S. Liu, M. Allati, H. Yang, X. Tu, Plasma reforming of biomass
533 gasification tars using mixed naphthalene and toluene as model compounds, *Energy*
534 *Convers. Manag.* 195 (2019) 409–419. doi:10.1016/j.enconman.2019.05.002.
- 535 [7] M. Craven, Y. Wang, H. Yang, C. Wu, X. Tu, Integrated gasification and non-thermal
536 plasma-catalysis system for cleaner syngas production from cellulose, *IOP SciNotes*. 1
537 (2020) 024001. doi:10.1088/2633-1357/aba7f6.
- 538 [8] H. Zhang, F. Zhu, X. Li, R. Xu, L. Li, J. Yan, X. Tu, Steam reforming of toluene and
539 naphthalene as tar surrogate in a gliding arc discharge reactor, *J. Hazard. Mater.* 369
540 (2019) 244–253. doi:10.1016/j.jhazmat.2019.01.085.
- 541 [9] A.N. Trushkin, M.E. Grushin, I. V. Kochetov, N.I. Trushkin, Y.S. Akishev,
542 Decomposition of toluene in a steady-state atmospheric-pressure glow discharge,
543 *Plasma Phys. Reports*. 39 (2013) 167–182. doi:10.1134/S1063780X13020025.

- 544 [10] S.Y. Liu, D.H. Mei, M.A. Nahil, S. Gadkari, S. Gu, P.T. Williams, X. Tu, Hybrid
545 plasma-catalytic steam reforming of toluene as a biomass tar model compound over
546 Ni/Al₂O₃ catalysts, *Fuel Process. Technol.* 166 (2017) 269–275.
547 doi:10.1016/j.fuproc.2017.06.001.
- 548 [11] F. Saleem, A. Harvey, K. Zhang, Low temperature conversion of toluene to methane
549 using dielectric barrier discharge reactor, *Fuel*. 248 (2019) 258–261.
550 doi:10.1016/j.fuel.2019.02.137.
- 551 [12] F. Saleem, K. Zhang, A. Harvey, Temperature dependence of non-thermal plasma
552 assisted hydrocracking of toluene to lower hydrocarbons in a dielectric barrier
553 discharge reactor, *Chem. Eng. J.* 356 (2019) 1062–1069.
554 doi:10.1016/j.cej.2018.08.050.
- 555 [13] F. Zhu, H. Zhang, H. Yang, J. Yan, X. Li, X. Tu, Plasma reforming of tar model
556 compound in a rotating gliding arc reactor: Understanding the effects of CO₂ and H₂O
557 addition, *Fuel*. 259 (2020) 1–11. doi:10.1016/j.fuel.2019.116271.
- 558 [14] Y.N. Chun, C.S. Kim, K. Yoshikawa, Decomposition of benzene as a surrogate tar in a
559 gliding arc plasma, *Environ. Prog. Sustain. Energy*. 32 (2012) 837–845.
560 doi:10.1002/ep.11663.
- 561 [15] N. Gao, X. Wang, A. Li, C. Wu, Z. Yin, Hydrogen production from catalytic steam
562 reforming of benzene as tar model compound of biomass gasification, *Fuel Process.*
563 *Technol.* 148 (2016) 380–387. doi:10.1016/j.fuproc.2016.03.019.
- 564 [16] L. Mao, Z. Chen, X. Wu, X. Tang, S. Yao, X. Zhang, B. Jiang, J. Han, Z. Wu, H. Lu,
565 T. Nozaki, Plasma-catalyst hybrid reactor with CeO₂/γ-Al₂O₃ for benzene
566 decomposition with synergetic effect and nano particle by-product reduction, *J.*
567 *Hazard. Mater.* 347 (2018) 150–159. doi:10.1016/j.jhazmat.2017.12.064.

- 568 [17] Z. Wu, J. Wang, J. Han, S. Yao, S. Xu, P. Martin, Naphthalene decomposition by
569 dielectric barrier discharges at atmospheric pressure, *IEEE Trans. Plasma Sci.* 45
570 (2017) 154–161. doi:10.1109/TPS.2016.2632154.
- 571 [18] L. Liu, Y. Liu, J. Song, S. Ahmad, J. Liang, Y. Sun, Plasma-enhanced steam reforming
572 of different model tar compounds over Ni-based fusion catalysts, *J. Hazard. Mater.* 377
573 (2019) 24–33. doi:10.1016/j.jhazmat.2019.05.019.
- 574 [19] D. Mei, S. Liu, Y. Wang, H. Yang, Z. Bo, X. Tu, Enhanced reforming of mixed
575 biomass tar model compounds using a hybrid gliding arc plasma catalytic process,
576 *Catal. Today*. 337 (2019) 225–233. doi:10.1016/j.cattod.2019.05.046.
- 577 [20] Y.N. Chun, S.C. Kim, K. Yoshikawa, Destruction of anthracene using a gliding arc
578 plasma reformer, *Korean J. Chem. Eng.* 28 (2011) 1713–1720. doi:10.1007/s11814-
579 011-0162-x.
- 580 [21] X. Kong, H. Zhang, X. Li, R. Xu, I. Mubeen, L. Li, J. Yan, Destruction of toluene,
581 naphthalene and phenanthrene as model tar compounds in a modified rotating gliding
582 arc discharge reactor, *Catalysts*. 9 (2019) 6–9. doi:10.3390/catal9010019.
- 583 [22] L. Liu, Q. Wang, S. Ahmad, X. Yang, M. Ji, Y. Sun, Steam reforming of toluene as
584 model biomass tar to H₂-rich syngas in a DBD plasma-catalytic system, *J. Energy Inst.*
585 91 (2018) 927–939. doi:10.1016/j.joei.2017.09.003.
- 586 [23] B. Xu, J. Xie, H. Zhan, X. Yin, C. Wu, H. Liu, Removal of toluene as a biomass tar
587 surrogate in a catalytic nonthermal plasma process, *Energy and Fuels*. 32 (2018)
588 10709–10719. doi:10.1021/acs.energyfuels.8b02444.
- 589 [24] Z. Wu, Z. Zhu, X. Hao, W. Zhou, J. Han, X. Tang, S. Yao, X. Zhang, Enhanced
590 oxidation of naphthalene using plasma activation of TiO₂/diatomite catalyst, *J. Hazard.*
591 *Mater.* 347 (2018) 48–57. doi:10.1016/j.jhazmat.2017.12.052.

- 592 [25] Y.C. Yang, Y.N. Chun, Naphthalene destruction performance from tar model
593 compound using a gliding arc plasma reformer, *Korean J. Chem. Eng.* 28 (2011) 539–
594 543. doi:10.1007/s11814-010-0393-2.
- 595 [26] C.M. Du, J.H. Yan, B. Cheron, Decomposition of toluene in a gliding arc discharge
596 plasma reactor, *Plasma Sources Sci. Technol.* 16 (2007) 791–797. doi:10.1088/0963-
597 0252/16/4/014.
- 598 [27] L. Yu, X. Li, X. Tu, Y. Wang, S. Lu, J. Yan, Decomposition of naphthalene by dc
599 gliding arc gas discharge, *J. Phys. Chem. A*. 114 (2010) 360–368.
600 doi:10.1021/jp905082s.
- 601 [28] T. Nunnally, A. Tsangaris, A. Rabinovich, G. Nirenberg, I. Chernets, A. Fridman,
602 Gliding arc plasma oxidative steam reforming of a simulated syngas containing
603 naphthalene and toluene, *Int. J. Hydrogen Energy*. 39 (2014) 11976–11989.
604 doi:10.1016/j.ijhydene.2014.06.005.
- 605 [29] F. Zhu, X. Li, H. Zhang, A. Wu, J. Yan, M. Ni, H. Zhang, A. Buekens, Destruction of
606 toluene by rotating gliding arc discharge, *Fuel*. 176 (2016) 78–85.
607 doi:10.1016/j.fuel.2016.02.065.
- 608 [30] P. Jamróz, W. Kordylewski, M. Wnukowski, Microwave plasma application in
609 decomposition and steam reforming of model tar compounds, *Fuel Process. Technol.*
610 169 (2018) 1–14. doi:10.1016/j.fuproc.2017.09.009.
- 611 [31] J. Sun, Q. Wang, W. Wang, K. Wang, Plasma catalytic steam reforming of a model tar
612 compound by microwave-metal discharges, *Fuel*. 234 (2018) 1278–1284.
613 doi:10.1016/j.fuel.2018.07.140.
- 614 [32] M. Młotek, B. Ulejczyk, J. Woroszył, K. Krawczyk, Decomposition of Toluene in
615 Coupled Plasma-Catalytic System, *Ind. Eng. Chem. Res.* 59 (2020) 4239–4244.
616 doi:10.1021/acs.iecr.9b04330.

- 617 [33] K. Tao, N. Ohta, G. Liu, Y. Yoneyama, T. Wang, N. Tsubaki, Plasma enhanced
618 catalytic reforming of biomass tar model compound to syngas, *Fuel*. 104 (2013) 53–
619 57. doi:10.1016/j.fuel.2010.05.044.
- 620 [34] S.Y. Liu, D.H. Mei, Z. Shen, X. Tu, Nonoxidative conversion of methane in a
621 dielectric barrier discharge reactor: Prediction of reaction performance based on neural
622 network model, *J. Phys. Chem. C*. 118 (2014) 10686–10693. doi:10.1021/jp502557s.
- 623 [35] X. Zhu, S. Liu, Y. Cai, X. Gao, J. Zhou, C. Zheng, X. Tu, Post-plasma catalytic
624 removal of methanol over Mn - Ce catalysts in an atmospheric dielectric barrier
625 discharge, *Appl. Catal. B, Environ.* 183 (2016) 124–132.
626 doi:10.1016/j.apcatb.2015.10.013.
- 627 [36] I. Istadi, N.A.S. Amin, Modelling and optimization of catalytic-dielectric barrier
628 discharge plasma reactor for methane and carbon dioxide conversion using hybrid
629 artificial neural network-genetic algorithm technique, *Chem. Eng. Sci.* 62 (2007)
630 6568–6581. doi:10.1016/j.ces.2007.07.066.
- 631 [37] T. Chang, J. Lu, Z. Shen, Y. Huang, D. Lu, X. Wang, J. Cao, R. Morent, Simulation
632 and optimization of the post plasma-catalytic system for toluene degradation by a
633 hybrid ANN and NSGA-II method, *Appl. Catal. B Environ.* 244 (2019) 107–119.
634 doi:10.1016/j.apcatb.2018.11.025.
- 635 [38] Z. Ye, J. Yang, N. Zhong, X. Tu, J. Jia, J. Wang, Tackling environmental challenges in
636 pollution controls using artificial intelligence: A review, *Sci. Total Environ.* 699
637 (2020) 134279. doi:10.1016/j.scitotenv.2019.134279.
- 638 [39] Y. Sun, L. Liu, Q. Wang, X. Yang, X. Tu, Pyrolysis products from industrial waste
639 biomass based on a neural network model, *J. Anal. Appl. Pyrolysis*. 120 (2016) 94–
640 102. doi:10.1016/j.jaap.2016.04.013.

- [40] A.J. Smola, B. Schölkopf, A tutorial on support vector regression, Stat. Comput. 14 (2004) 199–222. doi:10.1023/B:STCO.0000035301.49549.88.
- [41] H. Drucker, C.J.C. Surges, L. Kaufman, A. Smola, V. Vapnik, Support vector regression machines, Adv. Neural Inf. Process. Syst. 1 (1997) 155–161.
- [42] S.R. Safavian, D. Landgrebe, A Survey of Decision Tree Classifier Methodology, IEEE Trans. Syst. Man Cybern. 21 (1991) 660–674. doi:10.1109/21.97458.
- [43] Y. Shao, R.S. Lunetta, Comparison of support vector machine, neural network, and CART algorithms for the land-cover classification using limited training data points, ISPRS J. Photogramm. Remote Sens. 70 (2012) 78–87. doi:10.1016/j.isprsjprs.2012.04.001.
- [44] D. Mei, Y. He, S. Liu, J. Yan, X. Tu, Optimization of CO₂ conversion in a cylindrical dielectric barrier discharge reactor using design of experiments, Plasma Process. Polym. 13 (2016) 544–556. doi:10.1002/ppap.201500159.

Graphic abstract

